

## TEMPERATURE CALIBRATION OF EVOLVED GAS ANALYSIS\*

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### ABSTRACT

The problem of standardization of the temperature axis in evolved gas analysis is considered. The concept of using a precise reaction such as melting to trigger the evolution of a trace quantity of dissolved gas is studied by investigating  $\text{CO}_2$  dissolved in  $\text{K}_2\text{SO}_4$ . A precise gas evolution peak coincides with melting and is independent of the heating rate and the oxygen content of the atmosphere. Therefore,  $\text{CO}_2$  dissolved in  $\text{K}_2\text{SO}_4$  should be considered a possible candidate for a standardization material. A precise reaction acting to trigger a gas evolution peak is a useful approach to standardization of evolved gas analysis.

### INTRODUCTION

Interest in standardization of thermal analysis techniques in the various laboratories around the world has been increasing during the past few years<sup>1,2</sup>. Most of the efforts have been directed to developing standard materials for calibrating the temperature axis of differential thermal analysis. In contrast with the significant progress in this area, no experimental work on the standardization of evolved gas analysis has been published. This paper reports on an initial effort to develop a material for temperature calibration of evolved gas analysis.

The objective is to develop a material having a temperature calibration point during evolved gas analysis which is insensitive to changes in atmosphere and heating rate. Unfortunately, due to the law of mass action, most reactions which evolve a gas are sensitive to atmosphere and pressure changes and are ruled out on this basis. Considering the high sensitivity of gas detectors used in evolved gas analysis, only a small quantity of gas evolution is needed for standardization. Therefore, it seems reasonable to search for a material which undergoes a precise reaction which may be made to trigger the evolution of a small quantity of gas, even though the main reaction does not involve a gas. For example, a trace quantity of gas may be dissolved in a material which exhibits a precise melting point. Upon melting, the dissolved gas

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may be evolved, thus providing a standardization peak during evolved gas analysis. After preliminary screening of several materials,  $K_2SO_4$  was chosen for further study.

#### SAMPLE PREPARATION

Preliminary experiments indicate that carbon dioxide can be dissolved in  $K_2SO_4$  under a fairly wide range of conditions. Furthermore, the preparation conditions do not influence the evolved gas analysis curves obtained. The following procedure was arbitrarily chosen for subsequent sample preparation: Reagent Grade  $K_2SO_4$ \* was heated to  $1080^\circ\text{C}$  (slightly above the melting temperature) in a flowing  $\text{CO}_2$  atmosphere and held for one hour. While maintaining the  $\text{CO}_2$  atmosphere, the sample was then cooled to  $1000^\circ\text{C}$ , held for one hour to allow crystallization and then cooled to below  $500^\circ\text{C}$  before removing from the controlled atmosphere. The sample was then crushed and sieved on 40-mesh and 60-mesh screens. The 40- to 60-mesh fraction was retained and stored in a closed container until evolved gas analysis runs were made.

#### EXPERIMENTAL PROCEDURE

A platinum crucible containing a 100-mg sample is placed in a high purity aluminum oxide sample holder illustrated in Fig. 1. A platinum shell covers the alumina sample holder and a furnace\*\* is lowered over the platinum shell. The carrier

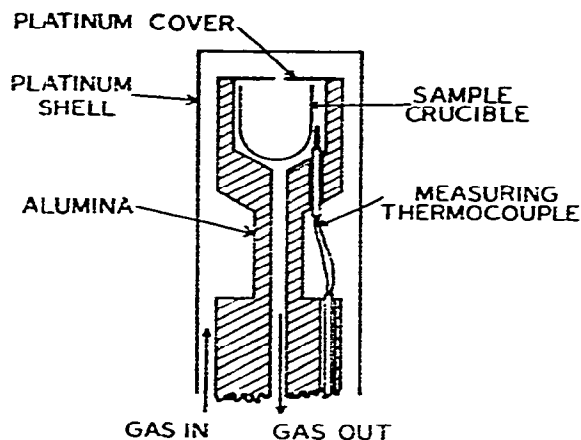


Fig. 1. Sample holder.

gas flows between the platinum shell and the alumina sample holder, up to the top of the sample holder and impinges on the top of the sample. The gas then passes around the crucible and through a 1/16-inch hole in the center of the sample holder to a gas

\*Mallinckrodt No. 7140.

\*\*Robert L. Stone, Model FI-C DTA furnace.

density detector\*, and subsequently to a mass spectrometer\*\*. The results reported here are from the density detector.

The gas volume between the sample and detector is quite small. The estimated lag time between the sample and detector for the 30 ml/min flow rate used in these experiments is less than six seconds. Generally, the measuring thermocouple is located next to the sample crucible. The measuring thermocouple is connected by way of an ice-junction to a laboratory potentiometer. Temperature event marks are made manually at approximately 10 before and 10°C after the evolved gas analysis peak of interest. The temperature of initial gas evolution is obtained by linear interpolation between these temperature marks. The temperature controller is connected to a separate control thermocouple (not shown in the figure) located in the hot zone between the platinum shell and alumina sample holder.

#### RESULTS AND DISCUSSION

Basically, three questions are to be answered with these experiments:

- (1) Is gas evolved during melting of the sample?
- (2) Does the heating rate influence the temperature of gas evolution?
- (3) Does the atmosphere influence the temperature of gas evolution?

Fig. 2 shows curves obtained to answer the first question. In this run the experimental procedure is modified by placing the measuring thermocouple bead directly in the sample and recording the output on the same chart which records the evolved

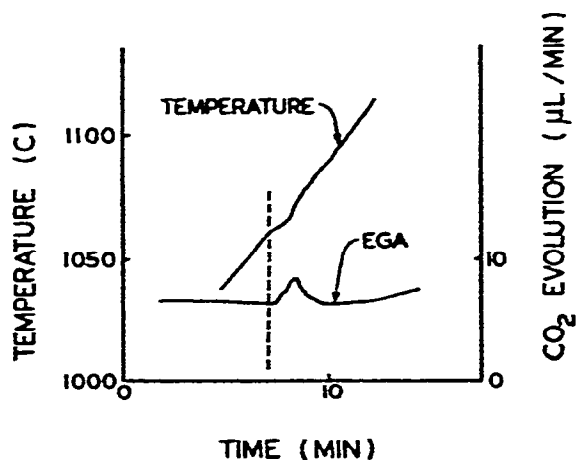


Fig. 2. Heating and evolved gas analysis curves.

gas analysis curve. The curves show that approximately 2  $\mu\text{l}$  (STP) of  $\text{CO}_2$  are evolved coinciding with the temperature arrest due to the heat of melting. The small shoulder

\*Gow-Mac, No. 140 (thermistor).

\*\*Associated Electrical Industries, Model MS-10.

which occurs in the evolved gas analysis curve before reaching the maximum is observed in most cases where gas is evolved during the melting of a granular material. This shoulder is believed to be due to a sudden decrease of exposed surface area which is caused by coalescence of the liquid.

Table I shows the temperature of initial gas evolution for a series of runs where the heating rate and atmosphere are varied. Heating rates of approximately 10 and 3°C/min and atmospheres of 100% N<sub>2</sub> and 20% O<sub>2</sub>-80% N<sub>2</sub> are used. These conditions are considered representative of those encountered in many evolved gas analysis studies, although other heating rates and atmospheres also are encountered.

TABLE I

EFFECT OF HEATING RATE AND ATMOSPHERE ON INITIAL PEAK TEMPERATURE

<i>Run no.</i>	<i>Heating rate (°C/min)</i>	<i>Atmosphere (% O<sub>2</sub>)</i>	<i>Initial peak temperature (°C)<sup>a</sup></i>	<i>Difference from mean (°C)</i>
70-53	10	0	1063	1.6
70-54	10	0	1063	1.6
70-55	10	0	1059	-2.4
70-56	10	0	1063	1.6
70-57	10	0	1063	1.6
70-58	10	0	1063	1.6
70-59	10	0	1063	1.6
70-61	3	0	1062	0.6
70-62	3	0	1060	-1.4
70-64	3	20	1057	-4.4
70-66	3	20	1060	-1.4
70-67	3	0	1061	-0.4

<sup>a</sup>Mean = 1061.4; standard deviation = 2.0.

A mean value of 1061.4°C with a standard deviation of 2.0°C was obtained for these runs. Statistical analysis indicates that the heating rate has no significant influence on the results but that the atmosphere might have minor significance.

A second series of runs was made at a later date (Table II) to recheck the possible significance of atmosphere. These runs gave a mean value of 1073.7°C with a standard deviation of 1.2°C. The relatively large difference of 12°C between the mean values for the two series of runs indicates that a significant change in the experimental conditions occurred between these two series. Such a change was not too surprising since the apparatus was used for numerous other runs between the two series and an uncalibrated thermocouple was used. The possibility that sample storage time affects the results should be carefully checked before final acceptance, although no effect of storage for several months was apparent in the preliminary screening experiments. Fortunately, in spite of the difference between the two series, the objective of the second series was met. Analysis of these results failed to confirm the minor significance of atmosphere suggested by the earlier runs.

Also, the possibility that dissolved CO<sub>2</sub> influenced the melting temperature was

TABLE II  
EFFECT OF ATMOSPHERE ON INITIAL PEAK TEMPERATURE

Run no.	Heating rate (°C/min)	Atmosphere (% O <sub>2</sub> )	Initial peak temperature (°C) <sup>a</sup>	Difference from mean (°C)
70-98	10	20	1073	-0.7
70-99	10	0	1073	-0.7
70-100	10	20	1073	-0.7
70-101	10	0	1074	0.3
70-102	10	20	1073	-0.7
70-103	10	0	1076	2.3

<sup>a</sup>Mean = 1073.7; standard deviation = 1.2.

considered. Differential thermal analysis of samples with and without dissolved CO<sub>2</sub> produced similar melting peaks with no apparent difference in temperature. However, it should be noted that assignment of an absolute temperature to the evolved gas analysis peak was not an objective of this work.

#### CONCLUSIONS

These results show that the concept of using a reaction such as melting to trigger the evolution of a trace quantity of gas is a useful approach to the development of temperature standards for evolved gas analysis. Furthermore, CO<sub>2</sub> dissolved in K<sub>2</sub>SO<sub>4</sub> is released at the melting point and produces a well-defined peak. The temperature of the peak is not influenced by the heating rates and atmospheres (oxygen content) studied. These preliminary results suggest that K<sub>2</sub>SO<sub>4</sub> should be considered a possible candidate for evolved gas analysis temperature standardization. However, investigations of a wider range of conditions are required before final acceptance. In particular, studies of the effect of sample storage conditions and other atmospheres are needed.

#### DEDICATION

This work is dedicated to the memory of the late Robert L. Stone, who was my teacher, advisor and friend.

#### REFERENCES

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